

**CORRELATIONS BETWEEN SURFICIAL SULFUR AND A REE CRUSTAL ASSIMILATION SIGNATURE IN MARTIAN SHERGOTTITES.** J.H. Jones<sup>1</sup> and H. B. Franz<sup>2</sup>, <sup>1</sup>XI, NASA/JSC, Houston, TX 77058 (john.h.jones@nasa.gov), <sup>2</sup>CRESST, NASA/GSFC, Greenbelt, MD 20771

**Introduction:** Compared to terrestrial basalts, the martian shergottite meteorites have an extraordinary range of Sr and Nd isotopic signatures. In addition, the S isotopic compositions of many shergottites show evidence of interaction with the martian surface/atmosphere through mass-independent isotopic fractionations (MIF, positive, non-zero  $\Delta^{33}\text{S}$ ) that must have originated in the martian atmosphere, yet ultimately were incorporated into igneous sulfides (AVS — acid-volatile sulfur; [1]). These positive  $\Delta^{33}\text{S}$  signatures are thought to be governed by solar UV photochemical processes. And to the extent that S is bound to Mars and not lost to space from the upper atmosphere, a positive  $\Delta^{33}\text{S}$  reservoir must be mass balanced by a complementary negative reservoir.

There are two current explanations for the large spread in shergottite Sr and Nd isotopic compositions. The first model assumes that this isotopic diversity represents a martian mantle heterogeneity with respect to a KREEP-like component produced from the crystallization of a martian magma ocean [2]. The second model assumes that all shergottites originated from a very depleted mantle and that the observed Nd and Sr isotopic dispersion results from assimilation of an ancient, enriched basaltic crust [3].

Newly acquired S isotopic data [1], coupled with REE whole-rock analyses [4], serve to constrain these two disparate models. We introduce here a parameter  $\text{La}/\text{Sm}^*$  [ $(\text{La}/\text{Sm})_{\text{sample}}/(\text{La}/\text{Sm})_{\text{QUE}}$ ], a proxy for crustal assimilation, where QUE refers to QUE 94201, the shergottite with the smallest La/Sm ratio. In this notation, therefore, the  $\text{La}/\text{Sm}^*$  for QUE is unity (Fig. 1). And the AVS  $\Delta^{33}\text{S}$  of QUE is indistinguishable from chondritic.

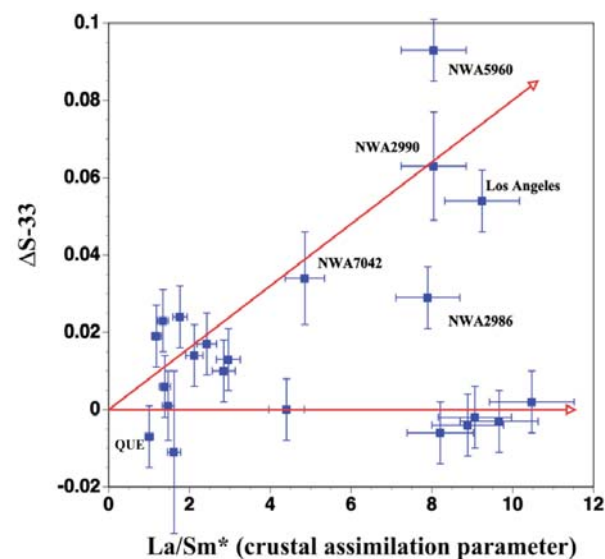
**$\Delta^{33}\text{S}$  vs.  $\text{La}/\text{Sm}^*$ :** Figure 1 shows that there are at least two distinct  $\Delta^{33}\text{S}$ - $\text{La}/\text{Sm}^*$  trends reflected in martian basalts. First, there is a trend of extremely variable  $\text{La}/\text{Sm}^*$  with no obvious change in  $\Delta^{33}\text{S}$ . A second trend shows a positive correlation between  $\Delta^{33}\text{S}$  and  $\text{La}/\text{Sm}^*$ . These trends constrain, for an individual shergottite, the amount of surficial MIF S that the rock has incorporated.

Some shergottites, with large amounts of lithophile crustal assimilants (high  $\text{La}/\text{Sm}^*$ ), have no  $\Delta^{33}\text{S}$  anomaly (e.g., Shergotty and Zagami), but *no* shergottites yet analyzed have yielded low  $\text{La}/\text{Sm}^*$  and high  $\Delta^{33}\text{S}$ . The latter observation is most consistent with a crustal assimilation model.

**Discussion:** The two models for the physical nature of the enriched component in shergottites make

very different predictions about the systematics of Fig. 1. If the enriched component resides in the mantle, there will be no correlation between  $\Delta^{33}\text{S}$  and  $\text{La}/\text{Sm}^*$ . Conversely, if the enriched component resides in the crust, those shergottites with the least crustal interaction would also be predicted to have the smallest  $\Delta^{33}\text{S}$  anomalies. Taken at face value, the systematics of Fig. 1 are much more consistent with a crustal reservoir being the enriched component.

Our physical interpretation of these observations is that positive  $\Delta^{33}\text{S}$  anomalies were produced in the atmosphere by UV irradiation and that these isotopically anomalous compounds eventually made their way to the martian surface. The speciation of this high- $\Delta^{33}\text{S}$  sulfur is unknown, but given the oxidized nature of the martian surface, we postulate that the high- $\Delta^{33}\text{S}$  sulfur was either oxidized or became oxidized. Fluids may then have incorporated this sulfur and transported it deeper into the crust. Some shergottites then assimilated this high- $\Delta^{33}\text{S}$  component on their ascent to the surface. The oxidized high- $\Delta^{33}\text{S}$  component was then reduced to sulfide, probably by oxidizing  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , but other redox reactions are also possible.



**Figure 1.**  $\Delta^{33}\text{S}$  vs.  $(\text{La}/\text{Sm})_{\text{sample}}/(\text{La}/\text{Sm})_{\text{QUE}}$ . Error bars are one-sigma [1]. All analyses are for AVS (sulfide) only. No sulfate analyses are represented here. Arrows are illustrative and are not regressions.

Another possibility for transferring a high  $\Delta^{33}\text{S}$  signature from an oxidized species to a reduced species is

isotopic exchange, without a bulk change of redox state. Sulfur in mantle-derived martian basalts is thought to be dominated by the sulfide species, not sulfate [5]. If isotopic exchange occurred between mantle-derived sulfide and assimilated sulfate, bulk conversion of sulfate to sulfide may not be necessary.

**Higher Order Terms.** Although we believe our physical model is reasonable, there are several features that suggest more complexity.

*First*, there are several shergottites with very modest La/Sm\* (~2-3) have a small  $\Delta^{33}\text{S}$  anomaly and larger than the  $\Delta^{33}\text{S}$  values of several highly enriched shergottites.

*Second*, Los Angeles, which is nearly indistinguishable in its Sr and Nd isotopic characteristics from Shergotty and Zagami, has a large  $\Delta^{33}\text{S}$  anomaly, whereas these latter shergottites have none. Clearly, there can be a decoupling between various crustal and surficial components during the assimilation process.

*Third*, the shergottites NWA 2990 and NWA 5960 are believed to be paired. And while both of these samples show large, positive  $\Delta^{33}\text{S}$  anomalies, the analyses do not agree within their  $1\sigma$  analytical errors. And while there would be a slight overlap of the  $2\sigma$  errors, there is a suggestion that the anomalous  $\Delta^{33}\text{S}$  component may be heterogeneously distributed at the hand-specimen scale.

*Fourth*, there is presently very little sulfur in the martian atmosphere. Therefore, current UV production of  $\Delta^{33}\text{S}$  anomalies is likely to be very inefficient. The easiest means of overcoming this problem is for there to have been more sulfur in the atmosphere at times in the past, perhaps during volcanic eruptions. However, accomplishing this probably requires a multi-stage process.

As noted above, mantle-derived sulfur is dominantly sulfide, not sulfate, and is generally much less volatile than oxidized sulfur species. Therefore, for large volumes of oxidized sulfur to be erupted by volcanism, mantle sulfide must first be oxidized. This is certainly possible if mantle-derived basalts assimilated oxidized crustal materials [e.g., 6], but volcanic outgassing of sulfur is not necessarily a given. Oxidation state must be specified.

We do note, however, that there is a substantial surficial reservoir of sulfur in the martian regolith. And solar UV should penetrate to the martian surface. But at present, we do not understand whether MIF reactions are likely for UV-solid interactions.

**Complementary reservoirs.** We noted above that mass balance probably requires a negative  $\Delta^{33}\text{S}$  reservoir to complement the positive reservoir observed in the shergottites.

**References:** [1] Franz H.B. et al. (2014) *Nature* **508**, 364-367. [2] Borg L.E. and Draper D.S. (2003) *Met. Planet. Sci.* **38**, 1713-1731. [3] Jones J.H. (2003) *Met. Planet. Sci.* **38**, 1807-1814. [4] Meyer C. (2012) Mars-Meteorite-Compendium. <http://curator.jsc.nasa.gov/antmet/mmc/>. [5] Righter K. et al. (2008) *Met. Planet. Sci.* **43**, 1709-1723. [6] Wadhwa M. (2001) *Science* **291**, 1527-1530.